CHAPTER V

DISCUSSIONS AND CONCLUSIONS

5.1 Discussions

5.1.1 Zinc perchlorate system

Table 5.1.1

Summary of Parameter Estimation-Aqueous $Zn(ClO_4)_2$

$\overset{\circ}{\Lambda}$ $cm^2\ \Omega^{-1}\ equiv^{-1}$	$\overset{\circ}{\lambda}_{Zn^{2+}}$ $cm^2\ \Omega^{-1}\ equiv^{-1}$	$\delta(\Lambda)$	comment
120.72	53.36	-	Onsager limiting law
121.29	53.93	-	Shedlovsky function
122.50	55.14	0.34	LW equation, present data
121.00	53.64	1.21	LW equation, DFK data (8)
122.70	55.34	-	Owen function, DFK data;assume ion-pair
120.55	53.19	-	Owen function, DFK data,assume complete dissociate

$\overset{\circ}{\lambda}_{ClO_4^-} = 67.36\ cm^2\ \Omega^{-1}\ equiv^{-1}$ (29, 30)

A summary of the results for aqueous $Zn(ClO_4)_2$ system is given in Table 5.1.1. Using the present data, the Lee and Wheaton equation (LW equation) gave a better fit with $\delta(\Lambda) = 0.34$ than that obtained from Dye, Faber and Karl data (DFK data) with $\delta(\Lambda) = 1.21$. The $\overset{\circ}{\lambda}_{Zn^{2+}}$ value (55.14 $cm^2\Omega^{-1}$ $equiv.^{-1}$) obtained from the present data is however, higher than that obtained by using Dye, Faber and Karl data (53.64 $cm^2\Omega^{-1}$ $equiv^{-1}$). Using the Owen function, Dye Faber and Karl fit their data and obtained $\overset{\circ}{\lambda}_{Zn^{2+}}$ value of 55.34 $cm^2\Omega^{-1}$ $equiv.^{-1}$

which is much higher than the value of 52.8 $cm^2\Omega^{-1}$ $equiv^{-1}$ obtained by Owen & Gurry (10) from their data on zinc sulfate using the assumption of ion-pair formation. If ion-pair formation was not assumed, however, the $\lambda^{\circ}_{Zn^{2+}}$ value of 53.19 $cm^2\Omega^{-1}$ $equiv^{-1}$ was obtained. Using Dye, Faber and Karl data, the $\lambda^{\circ}_{Zn^{2+}}$ value (53.64 $cm^2\Omega^{-1}$ $equiv.^{-1}$) obtained from the Lee and Wheaton equation is in agreement with that obtained from the Owen function (53.19 $cm^2\Omega^{-1}$ $equiv.^{-1}$). The $\lambda^{\circ}_{Zn^{2+}}$ value obtained from graphical analyses using the Onsager and the Shedlovsky extrapolation function (the first and the second row of Table 5.1.1) are also in reasonable agreement with these $\lambda^{\circ}_{Zn^{2+}}$ values.

5.1.2 Zinc sulfate system

Table 5.1.2

Summary of Parameter Estimation-Aqueous $ZnSO_4$

Λ° $cm^2\Omega^{-1}$ $equiv^{-1}$	$\lambda^{\circ}_{Zn^{2+}}$ $cm^2\Omega^{-1}$ $equiv^{-1}$	K_A $kg\ mol^{-1}$ or $dm^3\ mol^{-1}$	$\sigma(\Lambda)$	comment
133.47	53.45	-	-	Onsager limiting law
132.50	52.48	-	-	Shedlovsky function
132.13	52.11	140	0.18	LW equation, present data
134.08	54.06	165*	0.09	LW equation, Katayama data(11)
132.18	52.16	125	0.12	LW equation, Owen & Gurry data(10)
134.30	54.28	165	-	F-O equation, Katayamadata(11)
133.02	52.80	204	-	Fuoss & Shedlovsky Function, Owen & Gurry data(10) .

$\lambda^{\circ}_{SO_4^{2-}}$ = 80.02 $cm^2\Omega^{-1}$ $equiv.^{-1}$ (31)

* refers to fixed parameter

A summary of the results for aqueous $ZnSO_4$ system is given in Table 5. The results obtained from graphical analyses using the Onsager and the Shedlovsky extrapolation function are given in the first and the second row of Table 5.1.2. Due to the non-linear extrapolation of the Shedlovsky function $\Lambda^{\circ\prime}$, the resulting $\Lambda^{\circ}_{ZnSO_4}$ and thus $\lambda^{\circ}_{Zn^{2+}}$ would involve considerable uncertainty. Using the Lee and Wheaton equation, Katayama data gave a better fit with $\sigma(\Lambda) = 0.09$ compared with those obtained from the present data ($\sigma(\Lambda) = 0.18$) and Owen & Gurry data ($\sigma(\Lambda) = 0.12$). The $\lambda^{\circ}_{Zn^{2+}}$ values obtained from Owen&Gurry data (52.16 $cm^2\ \Omega^{-1}\ equiv^{-1}$) and the present data (52.11 $cm^2\ \Omega^{-1}\ equiv.^{-1}$) are in good agreement but they are lower than that obtained from Katayama data (54.06 $cm^2\ \Omega^{-1}\ equiv^{-1}$). The association constant obtained from Owen & Gurry data (125 kg mol^{-1}) is lower than those obtained from the present data (140 kg mol^{-1}) and Katayama data (165 kg mol^{-1}). Using Katayama data, the $\lambda^{\circ}_{Zn^{2+}}$ value obtained from the Lee and Wheaton equation (54.0 $cm^2\ \Omega^{-1}\ equiv.^{-1}$) is in reasonable agreement with that obtained from the Fuoss-Onsager equation (54.28 $cm^2\ \Omega^{-1}\ equiv^{-1}$). Owen and Gurry used the Fuoss extrapolation function and the Shedlovsky extrapolation function to fit their data. Both functions gave the same $\lambda^{\circ}_{Zn^{2+}}$ values of 52.80 $cm^2\ \Omega^{-1}\ equiv^{-1}$, $\Lambda^{\circ}_{ZnSO_4}$ = 133.02 $cm^2\ \Omega^{-1}\ equiv.^{-1}$ with K_A = 204 $dm^3\ mol^{-1}$. This $\lambda^{\circ}_{Zn^{2+}}$ (52.80 $cm^2\ \Omega^{-1}\ equiv^{-1}$) is though not much higher than that obtained from the Lee and Wheaton equation (52.16 $cm^2\ \Omega^{-1}\ equiv^{-1}$), the K_A value obtained by the Fuoss and the Shedlovsky extrapolation functions (204 $dm^3\ mol^{-1}$) is nearly twice as large as that obtained from the Lee and Wheaton equation (125 kg mol^{-1}).

5.1.3 Zinc chloride system

Table 5.1.3

Summary of Parameter Estimation-Aqueous $ZnCl_2$

Λ° $cm^2\ \Omega^{-1}$ $equiv^{-1}$	$\lambda^{\circ}_{Zn^{2+}}$ $cm^2\ \Omega^{-1}$ $equiv^{-1}$	$\lambda^{\circ}_{ZnCl^+}$ $cm^2\ \Omega^{-1}$ $equiv^{-1}$	K_A kg mol^{-1}	$\sigma(\Lambda)$	comment
130.93	54.58	-	-	-	Onsager limiting law
130.00	53.65	-	-	-	Shedlovsky function
132.55	56.20	35$\pm$10	4.5	0.21	LW equation, present data
132.02	55.67	-	-	0.23	LW equation, present data (assume complete dissociate)

$\lambda^{\circ}_{Cl^-}$ = 76.35 $cm^2\ \Omega^{-1}\ equiv.^{-1}$ (27, 28)

A summary of the results for aqueous $ZnCl_2$ system is given in Table 5.1.3.Using the present data, the Lee and Wheaton equation provided the best fit with $\sigma(\Lambda) = 0.21$ at fixed value of the association constant (4.5 kg mol^{-1}) determined by Lutfullah & Dunsmore & Paterson (13). This gave $\lambda^{o}_{Zn^{2+}} = 56.20$ $cm^2 \Omega^{-1}$ $equiv^{-1}$, and $\lambda^{o}_{ZnCl^+}$ = 35 $cm^2 \Omega^{-1}$ $equiv^{-1}$. If complete dissociation was assumed for $ZnCl_2$ solution below 0.01 mol kg^{-1}, a lower $\lambda^{o}_{Zn^{2+}}$ value of 55.67 $cm^2 \Omega^{-1}$ $equiv^{-1}$ was obtained with similar $\sigma(\Lambda)$ (0.21 and 0.23). Table 4.3 showed that for $ZnCl_2$ solutions below 0.004 mol kg^{-1} the concentration of $ZnCl^+$ ions due to ion association was less than 2.5% of the total $ZnCl_2$ concentration. The solutions of $ZnCl_2$ with concentration below 0.004 mol kg^{-1} could then be regarded as complete dissociate. From the analysis, it was found that $\sigma(\Lambda)$ was not a sensitive function of $\lambda^{o}_{ZnCl^+}$, thus only an estimate of this parameter could be obtained. The $\lambda^{o}_{Zn^{2+}}$ values obtained from graphical analyses (54.58 $cm^2 \Omega^{-1}$ $equiv^{-1}$ and 53.65 $cm^2 \Omega^{-1}$ $equiv^{-1}$) were lower than those obtained from theoretical analyses.

5.1.4 Cadmium perchlorate system

Table 5.1.4

Summary of Parameter Estimate-Aqueous $Cd(ClO_4)_2$

Λ^{o} $cm^2 \Omega^{-1}$ $equiv^{-1}$	$\lambda^{o}_{\frac{1}{2}Cd^{2+}}$ $cm^2 \Omega^{-1}$ $equiv^{-1}$	$\sigma(\Lambda)$	comment
119.86	52.5	0.14	LW equation, Matheson data(14)
120.86	53.5*	0.43	LW equation, Matheson data(14)
120.86	53.5	-	Shedlovsky function, Matheson data(14)

* refers to fixed parameter

$\lambda^{o}_{ClO_4^-} = 67.36$ $cm^2 \Omega^{-1}$ $equiv^{-1}$ (29, 30)

Using Matheson data, the $\lambda^{\circ}_{Cd^{2+}}$ value obtained from the Lee and Wheaton equation (52.5 $cm^2 \Omega^{-1} equiv^{-1}$) is lower than that obtained by Matheson using the Shedlovsky extrapolation function (53.5 $cm^2\Omega^{-1}equiv^{-1}$). Fixing the $\lambda^{\circ}_{Cd^2}$ value at 53.5 $cm^2 \Omega^{-1}$ $equiv^{-1}$, the Lee and Wheaton equation gave a poorer fit with $\delta(\Lambda) = 0.43$ than that obtained by using tha best fit parameter ($\delta(\Lambda) = 0.14$)

5.1.5 Cadmium sulfate system

Table 5.1.5

Summary of Parameter Estimation-Aqueous $CdSO_4$

Λ° $cm^2 \Omega^{-1}$ $equiv^{-1}$	$\lambda^{\circ}_{Cd^{2+}}$ $cm^2 \Omega^{-1}$ $equiv^{-1}$	K_A $kg\ mol^{-1}$ or $dm^3\ mol^{-1}$	$\delta(\Lambda)$	comment
134.82	54.80	-	-	Onsager limiting law
132.65	52.63	-	-	Shedlovsky function
133.22	53.20	165	0.14	LW equation, present data
133.02	53.00	212*	0.07	LW equation, Katayama data (11)
133.15	53.13	212	-	F-O equation, Katayama data (11)

* refers to fixed parameter

$\lambda^{\circ}_{SO_4^{2-}}$ = 80.02 $cm^2 \Omega^{-1}$ $equiv.^{-1}$ (31)

A summary of the results for aqueous $CdSO_4$ system is given in Table 5.1.5.The results obtained from graphical analyses using the Onsager and the Shedlovsky extrapolation functionsare given in the first and the second row of Table 5.1.5.The Shedlovsky extrapolation to infinite dilution was non-linear. This gave considerable uncertainty in the value of $\Lambda^{\circ}_{CdSO_4}$ and thus $\lambda^{\circ}_{Cd^{2+}}$ value. Using the Lee and Wheaton equation, the $\lambda^{\circ}_{Cd^{2+}}$ values obtained from the present data (53.20 $cm^2\Omega^{-1}$ $equiv.^{-1}$) and from Katayama data (53.00 $cm^2\Omega^{-1}$ $equiv.^{-1}$) are in good agreement with that obtained by Katayama using the Fuoss-Onsager equation (53.13 $cm^2 \Omega^{-1}$ $equiv.^{-1}$). Katayama data, however, gave a better fit with $\sigma(\Lambda) = 0.07$ than that obtained by using the present data, $\sigma(\Lambda) = 0.14$. The value of K_A obtained from the present data (165 kg mol^{-1}) is much lower than that obtained from Katayama data (212 kg mol^{-1}).

5.2 Conclusions

The results of the theoretical analyses showed that the $\lambda^{\circ}_{Zn^{2+}}$ values obtained for $Zn(ClO_4)_2$, $ZnSO_4$ and $ZnCl_2$ systems were inconsistent. The discrepancies may arise from the limitations of the Lee and Wheaton equation being applicable to these systems. In some cases, different sets of data also gave different $\lambda^{\circ}_{Zn^{2+}}$ values. Particularly for $ZnSO_4$ which is an associated symmetrical electrolyte, different sets of data yeild inconsistent K_A values. For $ZnCl_2$, on the other hand, only the first association constant was assumed. This assumption used to determine the value of the first association constant for this system (13) may not be valid. Comparison of the transference number of $ZnCl_2$ and $CdCl_2$ systems would suggest that association constant for the formation of $ZnCl_3^-$ complex would have to be taken in to account. Since the $\lambda^{\circ}_{Zn^{2+}}$ value obtained for $Zn(ClO_4)_2$, $ZnSO_4$ and $ZnCl_2$ systems are in the range 53-55 $cm^2 \Omega^{-1}$ $equiv^{-1}$, 52-54 $cm^2 \Omega^{-1}$ $equiv^{-1}$ and 56 $cm^2 \Omega^{-1}$ $equiv^{-1}$, respectively. It is therefore not posible to draw definite conclusion on the value of $\lambda^{\circ}_{Zn^{2+}}$ and K_A for these systems. However, it would suggest that the $\lambda^{\circ}_{Zn^{2+}}$ value $= 54 \pm 2$ $cm^2 \Omega^{-1}$ $equiv^{-1}$ and $\lambda^{\circ}_{ZnCl^+} = 35 \pm 10$ $cm^2 \Omega^{-1}$ $equiv^{-1}$.

For $Cd(ClO_4)_2$ and $CdSO_4$ systems, the $\lambda^{\circ}_{Cd^{2+}}$ values are 52.5 $cm^2 \Omega^{-1}$ $equiv^{-1}$ and 53.0-53.2 $cm^2 \Omega^{-1}$ $equiv^{-1}$ respectively. Using the same theoretical analysis, Indaratna found that $\lambda^{\circ}_{Cd^{2+}}$ value is 53.94 $cm^2 \Omega^{-1}$ $equiv^{-1}$ for $CdCl_2$ system (3). These analyses suggest that the $\lambda^{\circ}_{Cd^{2+}}$ value $= 53 \pm 1$ $cm^2 \Omega^{-1}$ $equiv^{-1}$.

To obtain the fit with the same value of $\sigma(\Lambda)$, the values of $\lambda^{\circ}_{M^{2+}}$, R, K_A and $\lambda^{\circ}_{MCl^+}$ were found to range between 0.01-0.04 $cm^2 \Omega^{-1}$ $equiv^{-1}$, 0.04-0.10 Å, 2-3 kg mol^{-1} and 10 $cm^2 \Omega^{-1}$ $equiv^{-1}$, respectively. These results showed that $\sigma(\Lambda)$ is a sensitive function of $\lambda^{\circ}_{M^{2+}}$ and R values but is not highly dependent on the K_A value. It is also not a sensitive function of the $\lambda^{\circ}_{MCl^{+}}$ value, thus only an estimate of this parameter could be obtained. The resulting $\lambda^{\circ}_{ZnCl^{+}}$ value decreased with increasing R value. In most cases, the values of the parameters obtained from the analysis using the Lee and Wheaton equation are highly dependent on the conductance data. In particular the value of K_A can differ by about 20% for 2 sets of the experimental data. Precise conductance data will thus be neccessary for the analysis to obtained these parameters.

The Lee and Wheaton equation although provided a reasonably good fit for the systems studied, gave the $\lambda^{\circ}_{M^{2+}}$ (M = Zn, Cd) value which differed from system to system. This may arise from the nature of the model which in turn affects the boundary conditions used for the evaluation of the distribution functions involved in the derivation. The problem of "pseudo mass action" terms (6) arising from the retention of the full exponential form of the pair-distribution function f_{ji}, has been discussed by Lee and Wheaton and was briefly mentioned earlier. The author decided to drop the complete terms of $K(b_{ji})$. This may affect the results of the analyses for associated electrolytes. However it was later found that for unsymmetrical electrolytes, the evaluation of the exponential terms in the pair distribution function gave rise to a number of terms proportional to $(\beta\kappa)^3$ which was not realised earlier. The other terms proportional to $(\beta\kappa)^3$ which arise from the final exponential form of f_{ji} were therefore omitted as suggested by Wheaton (3) to avoid counting the effect of ion-paring twice. However, the choice of omitted terms is still arbitrary. This may affect the results of the analyses for unsymmetrical electrolytes. For MCl_2 which is an associated unsymmetrical electrolyte, the results could well have the combined effect. The results in Table 4.1 show that the values of $\lambda^{\circ}_{M^{2+}}$ for MCl_2 are considerable higher than those obtained for MSO_4 and $M(ClO_4)_2$ systems. This effect will be negligible for MSO_4 system which is an associated symmetrical electrolyte. For $M(ClO_4)_2$ which is the dissociated unsymmetrical electrolyte, on the other hand, "pseudo mass action" will not be applied. The results obtained from the theoretical analyses of MSO_4 and $M(ClO_4)_2$ systems by the Lee and Wheaton equation would thus be more reliable than those found for MCl_2 system.

It would therefore seems appropriate for future studies to confirm the conductance data of these electrolytes, particularly, for the very dilute solutions (1 X 10^{-3} mol dm^{-3}). The appropriate optimisation programm for the multiparameter curve fitting to be used for simultaneous determination of M^{2+} (or MCl^{+}), R, and K_A values may also be required for further analysis. The validity of the effect of dropping the complete "pseudo mass action" term from the conductance equation should also be further investigated.